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Atomic Scale Dynamics of a Two-Dimensional Gas-Solid Interface

by

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ATOMIC SCALE DYNAMICS OF A TWO-DIMENSIONAL GAS-SOLID INTERFACE

S. J. Stranick, M. M. Kamna, and P. S. Weiss*

We have imaged the interface between a two-dimensional molecular gas and a two-dimensional molecular solid using a low temperature ultrahigh vacuum scanning tunneling microscope. The solid consists of benzene molecules strongly bound to step edges on a Cu{111} surface. Benzene molecules on the Cu{111} terraces move freely as a two-dimensional gas at 77K. We observe exchange between the two phases at the interface and the transient occupation of well defined sites at this interface. On mesas of the Cu surface, the two-dimensional gas is held in a cage of the solid as in a two-dimensional nanometer scale gas bulb.

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The two-dimensional (2D) phase diagram for adsorbates on surfaces contains all the complexity of the more familiar three-dimensional analogues. Adsorbates can be found as two-dimensional gases, liquids and solids. Different two-dimensional structures are found as temperature and coverage are varied. Phase transitions have been studied by a variety of scattering and diffraction techniques (1). In this paper, we observe the atomic scale dynamics of the equilibrium at the interface of a 2D solid and a 2D gas. We are able to observe the motion of individual molecules at this interface as has never been possible for three-dimensional systems. We use a low temperature ultrahigh vacuum scanning tunneling microscope (STM) (2) to observe these dynamics for benzene molecules adsorbed on the Cu{111} surface.

Soon after the STM was invented, it was used to study the motion of surface adsorbates by analysis of the transient population of surface sites (3). Since then, STM data has been used to analyze the kinetics of motion of adsorbates and of features such as surface steps and vacancies (4-6). These measurements use many of the techniques earlier developed for quantifying motion on the atomic scale using field ion microscopy (7). For STM measurements of mobile adsorbates at high coverage, correlation techniques have been used to analyze images in order to determine favored adsorption sites, surface ordering, and interaction energies (8).

We have previously studied adsorption sites and their effects on STM images of isolated benzene molecules on Pt{111} at 4K (9). At such a low temperature the benzene is frozen in place and no motion is observed. Benzene molecules have also been imaged at room temperature when held fixed in various ordered overlayers by coadsorbed CO on Rh{111} (10). On both these surfaces benzene molecules lie flat, *i.e.* with the molecular plane parallel to the surface plane. Wolkow has used a low temperature STM to observe the diffusion and perhaps desorption into the vacuum of isolated benzene molecules on the Si{111} surface (11). In this paper we study the interactions of the adsorbed benzene molecules and the interface between their two-dimensional phases.

After initial electrochemical polishing and repeated sputtering and annealing cycles in ultrahigh vacuum we obtained a clean flat Cu{111} crystal surface. The freshly cleaned crystal was dosed to

saturation coverage at room temperature by bleeding a small amount of benzene gas through a sapphire leak valve into the vacuum chamber. The purity of the benzene was checked *in situ* using mass spectroscopy to verify that impurities and undesired wall reactions were negligible. After dosing, the room temperature Cu{111} sample was then rapidly lowered into a cryogenic ultrahigh vacuum STM chamber held at 77K or at 4K (2).

Previous studies by Bent and coworkers have shown that benzene adsorbs and desorbs molecularly on the Cu{111} surface (12). As for the close-packed Pt and Rh surfaces, the first monolayer of benzene adsorbs with the molecular plane parallel to the surface plane (12). From temperature-programmed desorption (TPD) of perdeutero (d_6 -) benzene on Cu{111} it is known that multilayer and monolayer coverages of benzene desorb from the surface below 250K. A high-temperature tail in the TPD spectrum extending to 300K is attributed to desorption from surface defect sites. Therefore, by dosing the Cu{111} crystal at room temperature with benzene, we preferentially populate defect sites on the surface.

Initial observations showed that at both 4K and 77K the monatomic step edges on the Cu{111} surface were indeed decorated by adsorbed benzene. These features were not present on the bare surface. STM images of the benzene covered surface recorded at 77K are shown in Figs. 1a and 1b. Both straight and meandering monatomic height steps are present on the Cu{111} surface (13). All the steps are decorated with benzene molecules. Because along straight steps benzene molecules order into well defined adsorption sites, we concentrate our analysis on these. At 77K the benzene molecules are mobile on the terraces. At 4K, as on Pt{111} (9), molecular diffusion is frozen out on the terraces as well, and we can show that for our method of dosing the surface coverage of benzene on the Cu{111} terraces ($>200\text{\AA}$ wide) is *ca.* 0.002 ± 0.001 monolayers (14).

That molecules stick at the step edges is not surprising (15). Even rare gases such as Xe preferentially bind to step edges on crystal surfaces (16). Here the stronger interactions of the molecules with adsorption sites along substrate steps leads to formation of a fixed two-dimensional solid layer at these sites. At 77K, benzene molecules remain mobile on the atomically flat terraces of

Cu{111} and behave as a 2D gas in dynamic equilibrium with the 2D molecular solid along the step edges. This interface is analogous to the behavior of solutions at electrode surfaces where at the metal-solution interface there exists a bound "specifically adsorbed" layer of solution that contributes to the double layer (17). At the metal-solution interface, it is postulated that the molecules from the solution are able to exchange with this bound layer. We observe an analogous situation in two dimensions on the surface of our Cu{111} crystal.

Initial scans of straight Cu steps on benzene-dosed Cu{111} at 77K reveal that there are two rows of benzene adsorbed at the step. An example is shown in Fig. 1b. A well defined row of benzene molecules lies below the step riser (indicated by arrow 1) and another lies above the step riser (indicated by arrow 2). These first two rows are held rigidly in place and form a two-dimensional solid of benzene molecules at the Cu{111} step edge. In addition, a "noisy" (or "phantom") line of molecules is adjacent to row 2 on the upper terrace (indicated by arrow 3). We interpret the instability in row 3 as due to molecules moving in and out of the preferred sites of this row. The molecules can move parallel to the interface (along row 3) or can desorb into the 2D molecular gas on the terrace and readsorb, thus setting up the dynamic equilibrium between the two phases.

We analyze these images to determine the fraction of time that the features attributed to the molecules are present in row 3. We set a threshold level in the topography at 2/3 the half maximum of a typical molecular feature. We record the fraction of the total number of pixels within the half width half maximum of the center of the adsorption site which are above this threshold level (18). Analyses of rows 1 and 2 indicate occupation of 0.99 ± 0.01 and 0.99 ± 0.02 , respectively. The row 3 adsorption sites chosen for analysis are determined as described below. Analysis of these "next" adsorption sites along row 3 indicate a fractional occupation of 0.09 ± 0.08 so long as the bias voltage is kept low (*i.e.* unperturbing values), $|V_{tip}| \leq 0.5V$ for tunneling currents of $I=100$ pA.

We are observing the beginnings of crystallization in two dimensions. Growth of C₆₀ films on the Cu{111} surface have also been shown to proceed from step edges (19). The step edge in each

case functions as an atomic scale nucleation site much as a scratch in the bottom of a beaker serves to precipitate crystals out of a supersaturated solution.

On raised terraces on the Cu{111} surface — mesas — the encircling 2D solid benzene confines the 2D molecular gas. Such a mesa is shown in the $50\text{\AA} \times 30\text{\AA}$ area of the Cu surface in Fig. 2, also recorded at 77K. The solid benzene circles the mesa. The two-dimensional gas molecules can slide back and forth on the mesa faster than the time scale of the STM imaging the surface. We note that this is the two-dimensional equivalent of a gas bulb 30\AA in length.

If perturbing bias voltages are reached, $|V_{\text{tip}}| \geq 0.9\text{V}$ for tunneling currents of $I=100\text{ pA}$ at 77K, the images of step edges are changed. Once this threshold is exceeded, the STM tip sweeps additional molecules to the edge of the molecular solid on the upper terrace above the step riser (if these are within the field imaged in the STM scan). At this point, we find row 3 substantially occupied and a fourth row becomes fractionally occupied as seen in Fig. 3a. A cross sectional view along these rows shown in Fig. 3b highlights the stability of rows 1 and 2 and the “noise” inherent in row 3. As can be seen in Fig. 3a, the molecules are often present for several line scans (horizontal in the image) and then disappear and reappear on the time scale of imaging (seconds per line scan). The partially occupied sites now evident in row 3 are those that were used for the analysis of the unperturbed interface above.

After moving molecules to the step edge, we once again analyze the occupation of the sites along the step edges by row using non-perturbing tunneling conditions. Inspection of images such as the one shown in Fig. 3a reveals that a fourth row is also present for a smaller fraction of the time. The occupation fractions at the edge of the 2-D solid after sweeping molecules to the step edge are: 1.00 ± 0.01 for row 1, 0.97 ± 0.04 for row 2, 0.76 ± 0.10 for the row 3, and 0.07 ± 0.02 for row 4.

Note that the outermost row has comparable density whether it is attached to row 2 before sweeping molecules to the step edge or it is attached to row 3 afterwards. This is an indication that the interactions which cause 2D gas molecules to adsorb at the 2D solid interface are intermolecular rather than due to the step edge proximity. Further evidence for this comes from close examination

of the perturbations of the surface electronic structure by the step edge (20) and by the molecules. This analysis will be the topic of a forthcoming publication (21).

In summary, we have observed the dynamic equilibrium between a two-dimensional molecular solid and a two-dimensional molecular gas. We observe the motion of molecules at the gas-solid interface in real time. When encircled by a two-dimensional solid, the molecular gas can be trapped in a nanometer scale area of the surface. This may allow independent study of these trapped molecules and their interactions with each other and with the tunneling electrons supplied by the STM tip. The electronic interactions that account for the adsorption sites along step edges are now being studied in further low temperature STM measurements (21).

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13. The straight steps have two different orientations: close-packed steps oriented in the $\langle 11\bar{2} \rangle$ direction, and microfacets of Cu{100} oriented nominally in the $\langle 0\bar{1}1 \rangle$ direction.

14. Since the mobility of molecules on terraces freezes out below 77K, the equilibrium population of molecules on terraces may be lower at this "freeze-out" temperature. Nevertheless, the benzene coverage on Cu{111} terraces at 4K and at 77K is very low for our deposition method.
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18. This method reduces the contribution of noise in imaging as the tip displacements are well under the (1/6 maximum) difference between the 1/3 maximum threshold value and the half maximum at the perimeter of the area analyzed. The uncertainties reported are one standard deviation when tens of observations of each equivalent site are averaged.
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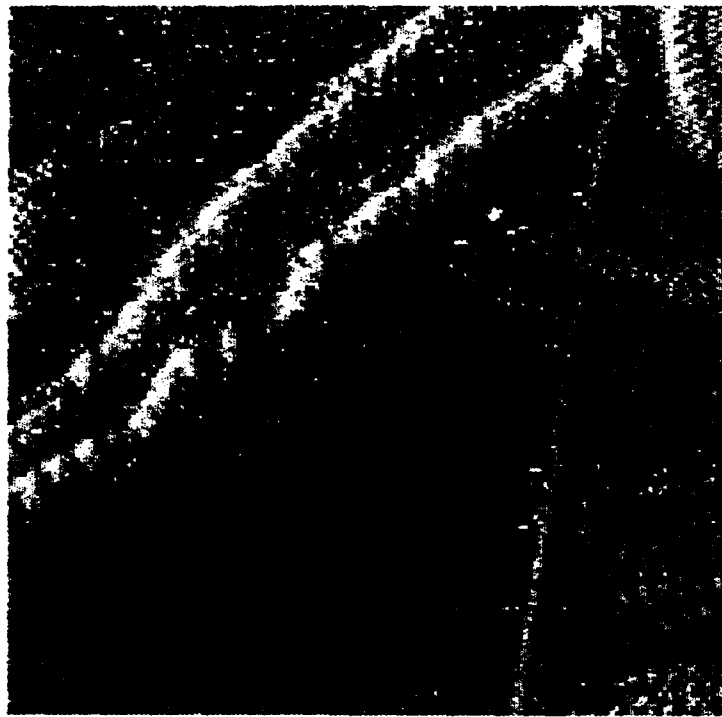
FIGURE CAPTIONS

1. Scanning tunneling microscope images showing of a Cu{111} surface with adsorbed benzene molecules. The molecules decorate the step edges in the form of a two-dimensional solid. The images were recorded at 77K in constant current mode. All images are unfiltered and were recorded at a tunneling current of 100 pA and a tip bias voltage of ~ 0.1 V.
 - a. A $200\text{\AA} \times 200\text{\AA}$ area showing straight and meandering substrate steps with the derivative along the horizontal axis displayed (as if the surface is illuminated from the left).
 - b. A topographic display of a $40\text{\AA} \times 40\text{\AA}$ area showing a decorated straight step edge.
2. A scanning tunneling microscope image showing a $50\text{\AA} \times 30\text{\AA}$ area of a Cu{111} surface recorded at 77K that includes a triangular mesa one atom higher than the surrounding terrace and approximately 30\AA long. The molecules of the two-dimensional solid entrap the two-dimensional gas. The gas molecules are apparent as streaks in the interior area of the mesa.
3.
 - a. A scanning tunneling microscope image recorded at 77K of the $40\text{\AA} \times 40\text{\AA}$ area shown in Fig. 1b (but rotated 90°) after the STM tip has intentionally swept additional molecules from the terrace to fill adsorption sites above the step riser. Two rows of benzene (3,4) now transiently occupy sites on the upper terrace adjacent to the 2D molecular benzene solid.
 - b. Cross sections along the rows marked in Fig. 3 show the static occupation of the sites in rows 1 and 2, above and below the step riser, respectively. Molecules in the row 3 undergo motion fast on the time scale of STM imaging (seconds). This can be seen from the rapid oscillation of the cross section for row 3 between topographic heights typical of occupied and unoccupied surface sites. Note that row 2 data are shifted by one-half the intermolecular spacing so as to align molecular features for all three rows.

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Fig. 1a

Up^



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Fig. 1b

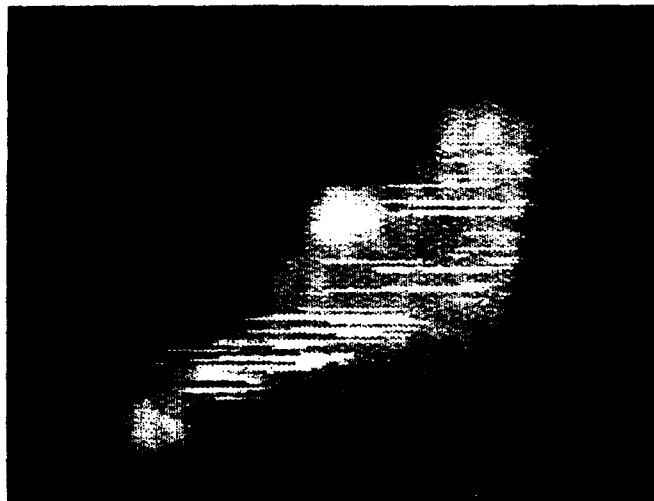
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Fig. 2

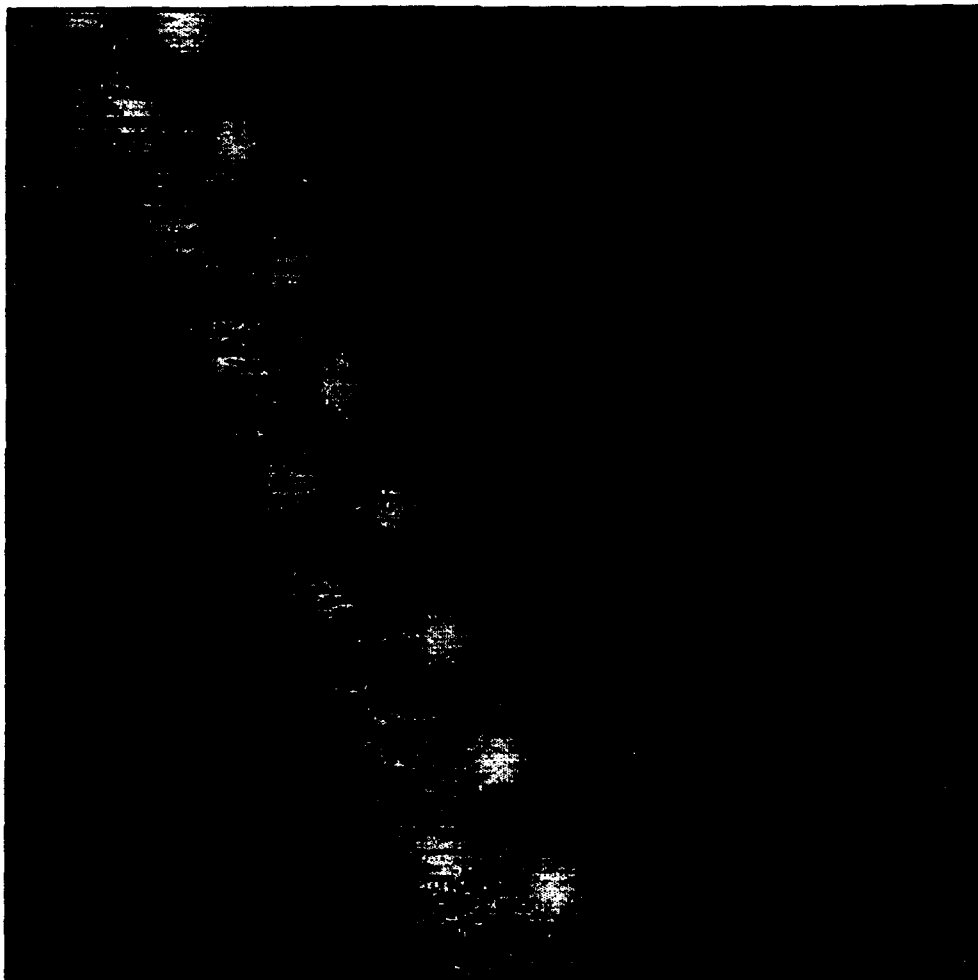
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Fig. 3a

Up^



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2

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1

